

AD-A258 788



2

MTL TR 92-62

AD

HIGH TEMPERATURE CHEMISTRY OF FIBERS AND COMPOSITES

DONALD R. MESSIER
CERAMICS RESEARCH BRANCH

DTIC
ELECTE
DEC 29 1992
S A D

September 1992

Approved for public release; distribution unlimited.

92-32855



US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY LABORATORY

92 12 28 030

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 92-62	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HIGH TEMPERATURE CHEMISTRY OF FIBERS AND COMPOSITES		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Donald R. Messier		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 SLCMT-EMC		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: ILI611102.AH42
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 20783-1145		12. REPORT DATE September 1992
		13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Presented on 8 January 1992 at the 16th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Fibers Composites Ceramics	Whiskers Silicon nitride Silicon carbide	Oxynitride glass High temperature chemistry
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (SEE REVERSE SIDE)		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 20

ABSTRACT

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form in situ composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.

FOREWORD

This report is the text of the James I. Mueller Memorial Lecture presented at the invitation of the Engineering Ceramics Division of the American Ceramic Society at the Sixteenth Conference on Composites and Advanced Ceramics in Cocoa Beach, FL on 8 January 1992. The lecture is dedicated to the memory of our late colleague and mentor, Dr. James I. Mueller. Some of his important contributions to what has become an outstanding annual meeting are summarized below.

The first "Cocoa Beach Meeting" attended by the author was the Fourth Conference on Composites and Advanced Ceramics in 1980. At that time, what now comprises two meetings, totaling six days of concurrent sessions over two weeks, was one meeting with single sessions. The 1980 conference program totaled 47 papers including one session of four papers on ceramic matrix composites. Dr. Mueller chaired the plenary session which at the fourth meeting consisted of only three papers. At that time, meetings of the Steering Committee, presided by Dr. Mueller, were held in his hotel room as they had been since the meeting's inception. In addition to these activities, Dr. Mueller also arranged for the speaker and presided at the banquet. The foregoing are just a few examples of Dr. Mueller's contributions, both big and small, to the origins of this conference, and it is no exaggeration to say that without the efforts of Dr. James I. Mueller there would be no Cocoa Beach Meeting.

DTIC QUALITY ASSURANCE

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

CONTENTS

	Page
FOREWORD	iii
INTRODUCTION	1
FIBERS AND WHISKERS	1
Carbide and Nitride Fibers	1
Carbide and Nitride Whiskers	3
Si ₃ N ₄ -BASED <u>IN SITU</u> COMPOSITES	3
Whisker-Reinforced Si ₃ N ₄ Materials	4
Sintered Si ₃ N ₄ with Oriented Microstructures	4
OXYNITRIDE GLASSES AND GLASS FIBERS	5
Oxynitride Glasses	5
Oxynitride Glass Fibers	6
CONCLUSIONS	7
ACKNOWLEDGMENTS	7
REFERENCES	22

INTRODUCTION

The fabrication and properties of ceramic fibers and composites, as well as oxynitride glasses, are often crucially affected by high temperature chemistry. For example, the high temperature performance of carbide and nitride fibers is limited by vapor phase and crystallization processes, and oxynitride glass and glass fiber properties are critically dependent upon decomposition reactions that occur during glass melting. On the plus side, advantage can be taken of high temperature chemistry to make in situ whisker/fiber composites and to produce materials with oriented microstructures. Whatever the case, improvement of process control invariably requires better understanding of process chemistry.

This report deals with three principal topics, all more or less related to silicon nitride, a long-standing interest of the author. The topics also represent areas in which the understanding and control of high temperature chemistry is critical. The first section of the paper, on carbide fibers and whiskers with high temperature properties suitable for ceramic-matrix composites (CMCs), draws from the author's experience on the Steering Committee of the DARPA-Dow Corning program on the development of advanced SiC fibers¹ and from a recently completed technology assessment trip to Japan.² The second part of the paper, which discusses in situ Si₃N₄-based composites, ties the author's earlier work on reaction bonded Si₃N₄ and on the kinetics of the α/β Si₃N₄ phase transformation to recent developments in this emerging technological area. The final part of the paper considers oxynitride glasses (the grain boundary phase in sintered Si₃N₄) and recent progress in improving the properties of oxynitride glass fibers, the topic of the author's current research.

FIBERS AND WHISKERS

As indicated in the Introduction, the discussion in this section is limited to fibers and whiskers of the type that could be considered for use as reinforcements in high performance CMCs. The discussion is further limited to materials comprised principally of SiC and Si₃N₄, the fiber and whisker compositions of greatest current interest for CMCs. With one exception, the fibers considered herein are derived from pyrolysis of fibers spun from organic precursors. The whiskers, on the other hand, are synthesized directly from high temperature reactions involving vapor phases.

Carbide and Nitride Fibers

Table 1 lists commercially available polymer-derived nitride and carbide fibers. The list is limited to small diameter (10 μm to 20 μm), uncoated continuous fibers of the type likely to be used in CMCs. Large diameter (100 μm or greater) filaments are unlikely to find extensive use in such composites and are, therefore, not included in this discussion. The fibers listed in Table 1 are all amorphous (or microcrystalline), nonstoichiometric, and contain significant amounts of oxygen (up to 10 wt% or more). All of the fibers are pyrolyzed to their final compositions at temperatures (1400°C or less) below which they are likely to be exposed to during ceramic processing. While glass-ceramic matrix composites have admittedly been successfully fabricated with "Nicalon" silicon carbide fibers by minimizing processing time at high temperatures,³ the types of fibers listed in Table 1 are thermally unstable and generally of limited utility for the fabrication of CMCs; processing of the latter more typically requires long hold times at high temperatures.

Table 1. COMMERCIALY AVAILABLE POLYMER-DERIVED CARBIDE AND NITRIDE CERAMIC FIBERS

Fiber	Precursor	Source	Remarks
Si-C-O	"Nicalon"	PCS	Nippon Carbon Co.
Si-N-C-O	"HPZ"	HPZ	Dow Corning Corp.
Si-N-O	"SNF"	PSZ	Tonen Corp.
Si-Ti-C-O	"Tyranno"	PTC	Ube Corp.

The high temperature instabilities of polymer-derived ceramic fibers result from several processes. The free carbon contained in carbide fibers generates thermal decomposition reactions such as the following:



Undesirable effects of such decomposition include reduction of fiber strength by formation of pores and channels, and also by formation of voids in the matrix if the latter contains a significant amount of glass.

When heated to temperatures above 1200°C, nitride fibers of the type in Table 1 are susceptible to oxygen uptake that results in substantial strength loss.

Furthermore, since all of the fibers under consideration are amorphous or poorly crystalline, heat treatment for significant times at above 1300°C or so induces crystallization. Formation of coarse crystalline grains also greatly reduces fiber strength.

In view of the above, it is evident that further development is needed to produce a continuous, polymer-derived, carbide or nitride ceramic fiber capable of retaining its properties under the rigorous fabrication conditions required for most CMCs. Ideally, the improved fiber would still be small in diameter (10 μm to 20 μm) but have enhanced high temperature stability. Required for improved fiber thermal stability are lower oxygen contents, stoichiometric chemical compositions (no excess C or O), and uniform, fine-grained crystalline microstructures.

Table 2 summarizes current activity along the guidelines suggested above on the development of carbide and nitride fibers with improved thermal stability. It is clear from Table 2 that the thermal stability problem is well recognized and receiving considerable attention as is indeed essential to progress in the development of viable fiber-reinforced CMCs.

Table 2. CARBIDE AND NITRIDE CERAMIC FIBERS UNDER DEVELOPMENT

Fiber	Precursor	Reference	Remarks
Si-C	PCS	4	Radiation cured, low O fiber. Retains strength at 1500°C.
Si-C	PCS, BSZ	5	Crystalline SiC. Excellent strength retention to 1600°C.
Si-B-N	PBSZ	6	Good high temperature strength and thermal stability.
Si-C	SiC	7	Sintered SiC. Good high temperature stability.
B-N	MAB	8	BN fiber with excellent high temperature properties.

NOTE: Glossary of Abbreviations in Tables 1 and 2; BSZ = Borosilazane; HPZ = Hydridopolysilazane; MAB = Methylaminoborazine; PBSZ = Polyborosilazane; PCS = Polycarbosilane; PSZ = Polysilazane; PTC = Polytitanocarbosilane; and SiC = Silicon carbide.

The high oxygen contents of many polymer-derived fibers stem from the air cure required to polymerize the precursor fibers. Approaches to the production of low oxygen polymer-derived fibers include changing to a radiation cure instead of an air cure,⁴ and using precursors that pyrolyze to low oxygen compositions.^{5,6,8} An alternative approach is to make fibers by sintering fibrous precursors of particulate, crystalline SiC.⁷ Strength loss from fiber crystallization can be minimized by making fibers that are crystalline and stoichiometric to begin with,^{5,7} or by the selection of compositions that resist crystallization when heated to high temperatures.^{6,8}

While it is encouraging that the problem of high temperature instability is well recognized and the subject of active research, fiber availability is a critical consideration to fabricators of CMCs. It is unlikely that any of the fibers listed in Table 2 will be commercially available in the next several years and, in any event, the extent of application of the fibers depends upon their being readily obtainable and affordable. A key to the latter considerations is the size of the market that develops for the fibers; something difficult to estimate at present. Therefore, while it is recognized that continuous fibers will always be needed for certain applications in which highly directional properties are required, it seems worthwhile to consider alternative composite systems, and the following discusses some of those alternative concepts.

Carbide and Nitride Whiskers

In contrast to the situation regarding continuous fibers, crystalline, stoichiometric, SiC, and Si₃N₄ whiskers are readily available commercially.⁹⁻¹¹ The whiskers are formed via inorganic vapor phase reactions similar to the following example for SiC:



Whiskers are typically 0.1 μm to 1.5 μm in diameter with aspect ratios (length/diameter) from 20 to 200. Additionally, the whiskers are stoichiometric and crystalline, giving them good high temperature stability. Significant problems, however, are difficulties in handling and incorporating whiskers into composites and, possibly even more important, the potential health hazards from dealing with such fine, sometimes dendritic materials. Discussed in the following section are some alternative approaches to obtaining materials with the advantages of whisker-reinforced structures but without the handling problems and health hazards associated with whiskers.

Si₃N₄-BASED IN SITU COMPOSITES

In the past few years interest has increased in alternative approaches to obtaining the benefits of composite-type microstructures without the problems of incorporation and achieving a uniform distribution of a second phase. Considered in this section are the formation of whiskers in situ in sintered or reaction bonded Si₃N₄, and the fabrication of sintered Si₃N₄ with oriented microstructures. Both of these approaches have been employed successfully to produce silicon nitride materials with fracture toughnesses and strengths comparable to those of composites fabricated from physical mixtures of components.

Whisker-Reinforced Si_3N_4 Materials

Figures 1 through 3, from an early study of the α/β Si_3N_4 transformation,^{12,13} illustrate an interesting phenomenon that has more recently been taken advantage of to fabricate sintered Si_3N_4 materials reinforced with SiC whiskers formed in situ.¹⁴⁻¹⁶ The SiC whiskers shown in the figures resulted from merely heating Si_3N_4 powder at 1600°C in a graphite crucible in oxygen-contaminated N_2 . As shown in Figure 3, no such whiskers appeared in Si_3N_4 powder heated for 10 hours at the same temperature in oxygen-free N_2 . A mechanism for the formation of SiC in Si_3N_4 (without reference to whiskers) had been proposed earlier by Colquhoun, et al.,¹⁷ and the chemistry of the process is illustrated in Figure 4. As shown in the figure, SiC whiskers form *via* the reaction of CO gas with the Si_3N_4 powder. One likely source of CO is reaction of residual O_2 in the system with the graphite crucible. Also, as suggested by Colquhoun et al., the SiO gas produced by the SiC-forming reaction can combine with C (from the crucible) to form additional CO. Considering that in the example shown the graphite crucible represents essentially an infinite sink for carbon, the reaction is self-sustaining as long as the Si_3N_4 remains at temperature.

As indicated above, several laboratories¹⁴⁻¹⁶ have reported success in forming in situ Si_3N_4 -matrix composites reinforced with SiC whiskers. In the references cited, the carbon source is C powder which is mixed with Si_3N_4 and SiO_2 to form the starting material. The powder mixtures are subsequently hot pressed to obtain dense composites. Whisker contents as high as 25 wt% have been realized by heat treatment for two hours at 1700°C .¹⁵ Song and Liu¹⁶ reported a modulus of rupture of 649 MPa and fracture toughness of $8.0 \text{ MPa}\cdot\text{m}^{1/2}$ for a hot-pressed composite containing 15 vol% SiC whiskers, both impressively high whatever the preparation method and indicative of the considerable potential of this family of materials.

Another possible but as yet unexploited approach to the fabrication of Si_3N_4 composites is illustrated in Figure 5.¹⁸ α - Si_3N_4 whiskers, such as the ones evident in the figure, are often observed in the nitridation of Si powder compacts to form reaction bonded Si_3N_4 (RBSN). The drops at the tips of the whiskers suggest that they formed via the VLS (Vapor-Liquid-Solid) mechanism first proposed by Wagner and Ellis¹⁹ for the growth of Si whiskers.

The likely VLS mechanism that applies to Si_3N_4 is illustrated in Figure 6. Scanning electron microscopy (SEM) analysis indicates that the liquid drop at the tip of the whisker is an iron silicide (Fe being a common contaminant in commercial Si powder),¹⁸ and the likely source of Si in the vapor phase is SiO gas. As illustrated in Figure 6, the gaseous reactants dissolve in the liquid to precipitate Si_3N_4 at the solid-liquid interface, thus providing a means of growing the extremely elongated crystals in Figure 5 and, potentially, an in situ composite type of microstructure. Figure 7 is a SEM photomicrograph of a RBSN specimen containing visible quantities of a fibrous phase and illustrating the possibility of forming a duplex Si_3N_4 microstructure.²⁰ While intriguing, no evidence exists to show that such microstructures provide significant toughening, and whether or not these duplex structures can be exploited to fabricate tough composites is an open question.

Sintered Si_3N_4 with Oriented Microstructures

Another interesting approach to the formation of composite-like Si_3N_4 bodies is to take advantage of the propensity of Si_3N_4 to form high aspect ratio grains under certain conditions. An example of the growth of high aspect ratio grains of β - Si_3N_4 from the liquid phase

is shown in Figure 8 from a study of the α/β Si_3N_4 phase transformation.¹³ That figure shows the development of elongated grains in Si_3N_4 powder heated with MgO for various lengths of time at 1600°C. Figure 9 illustrates, schematically, the process through which the columnar grains formed.

While clearly different from the VLS mechanism discussed above, the solid-liquid process shown in Figure 9 produces a similar result; i.e., high aspect ratio crystals. Moreover, it is well documented in the literature on crystal growth that the aspect ratio of such crystals depends upon the chemistry of the liquid from which they are grown,²¹ and full advantage of this behavior has been taken by Pyzik and coworkers to produce "self-reinforced Si_3N_4 " with impressive properties.²²⁻²⁴ That group has already reported the fabrication of pressure sintered Si_3N_4 bodies with bend strengths of 1200 MPa and fracture toughness, K_{IC} , values of 10 $\text{MPa}\cdot\text{m}^{1/2}$ (as compared to around 5 $\text{MPa}\cdot\text{m}^{1/2}$ for material without preferred orientation). Clearly, this approach has great potential for the production of composite-like microstructures without the need for mixing separate components, and this research area is deservedly one of considerable current interest.

OXYNITRIDE GLASSES AND GLASS FIBERS

The author's current research on oxynitride glasses²⁵ originated from interest in examining in detail the properties of the glassy grain boundary phase in sintered Si_3N_4 . In view of the outstanding properties of the latter material, and considering that fracture was known to be intergranular in sintered Si_3N_4 , it was felt that the grain boundary glass would be an interesting material in its own right. Furthermore, the properties and high temperature chemistry of the glass are relevant to Si_3N_4 technology and, thus, a logical subject for inclusion in this paper.

Oxynitride Glasses

Figure 10, after Risbud,²⁶ schematically shows the structure of an oxynitride glass and illustrates why the properties of the glass are enhanced by the substitution of N for O in the glass structure. While the details require further investigation, this undoubtedly oversimplified picture shows that the substituted N is bonded to three Si atoms rather than two as is the case for O. The result is tighter structure and a glass that is harder and has an increased elastic modulus; also, the melting temperature and density increase although the increase in modulus is considerably more than would be expected from the density increase. Additional advantages of oxynitride glasses are considered elsewhere,²⁷ and it is now well established that such glasses have the potential for providing properties superior to any known oxide glasses. In accordance with the theme of this paper, however, the realization of that potential requires a better understanding and control of the high temperature chemistry of oxynitride glass systems.

A major problem with oxynitride glasses of any composition is illustrated by Figure 11 showing two large disks of Y-Si-Al-O-N glass. The glass from which both specimens originated was made in a hot isostatic press under high N_2 pressure.²⁸ While one disk is obviously very clear and transparent, the other exhibits black cloudy areas. Extensive optical microscopy on various oxynitride glasses has shown that the black clouds consist of metallic inclusions similar to those apparent in the photomicrographs in Figure 12. The inclusions have been shown by SEM to be Si-rich often containing Fe when the latter is present as an impurity in the glass.²⁹ In more recent glasses with improved purity and homogeneity, the

inclusions are finer and more uniformly distributed giving the glass a uniform grey color. In addition to reducing transparency, the metallic inclusions represent strength limiting defects in the glass; the latter being particularly significant in the oxynitride glass fibers discussed below.

These colloidal, Si-rich metallic defects, while a key problem in oxynitride glasses, and possibly of significant influence in the glassy, grain boundary phase in sintered Si_3N_4 as well, have received scant attention in the literature. The most significant observations on the subject were made by Kelen and Mulfinger³⁰ who, based upon their studies of the solution of N in glass, and also on earlier work by Zintl,³¹ and by Geld and Esin,³² proposed the mechanism illustrated in Figure 13 for the formation of colloidal Si precipitates in glass. Interestingly, this phenomenon has little if anything to do with the presence of N in the glass. It merely reflects the fact that the glass is produced in a highly reducing atmosphere. Under such conditions, oxygen loss from the melt results in the formation of divalent Si which appears to be stable in solution at high temperatures. As shown in Figure 13, however, when the glass is cooled the divalent Si disproportionates into tetravalent Si and elemental Si; the latter condensing as colloidal precipitate particles.

Oxynitride Glass Fibers

The potential advantages of oxynitride glasses over conventional oxide glasses have led to interest by the U.S. Army in the possible use of oxynitride glass fibers in high performance composites. A potential application of such composites, a hull for an infantry fighting vehicle, is illustrated in Figure 14. An oxide glass fiber/resin matrix composite has already been successfully tested for that application, and oxynitride glass fibers could provide some of the additional advantages indicated in the figure. While impressively high elastic modulus values have been achieved for oxynitride glass fibers,²⁵ tensile strengths thus far obtained are unacceptably low for the type of composite shown in Figure 14. The key to improvement in fiber tensile strength is better understanding and control of the high temperature chemistry of glass, and fiber processing and recent progress along those lines is summarized below.

The apparatus employed for making oxynitride glass fibers at the U.S. Army Materials Technology Laboratory (MTL) is shown in Figure 15.³³ Recent efforts have been concentrated on making fibers from glasses in the system Mg-Si-Al-O-N. Glass compositions are similar to "S" glass (an Al-Mg-Si oxide) with 3 atomic % to 4 atomic % N substituted for some of the oxygen. Fibers are drawn from premelted glass contained in the molybdenum crucibles. The crucibles are inductively heated in N_2 to the drawing temperature of around 1550°C ; the exact temperature depending upon glass composition. Fibers as small as $8\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$ in diameter have been drawn at rates as high as 1500 m/min. The elastic moduli of the fibers range from 105 GPa to 110 GPa as compared to 85 GPa for "S" glass which is the highest performance commercially available oxide glass fiber.³⁴

As mentioned above, progress in improving the tensile strength of our oxynitride glass fibers has come mainly through understanding of process chemistry. Before process improvements, the fibers often failed from internal defects, one of which is shown in Figure 16. This fiber failed from a μm -sized inclusion identified by SEM as iron silicide. This type of defect, similar to the inclusions seen in Figure 12 and worsened by the presence of Fe impurities, was eliminated, and tensile strength consequently improved, by eliminating Fe contamination in the glass batch.

Although some earlier evidence indicated that glass quality was improved by batching with AlN rather than Si₃N₄, Figure 17 shows a fiber failure from an inclusion rich in Al. The latter probably came from unreacted Al in the AlN powder used to formulate the glass batch. This example, as well as the foregoing one about Fe, illustrates another consequence of melting the glass in a reducing atmosphere; the impurities remain metallic rather than being oxidized to metal ions as would be the case for melting in air.

Increases in oxynitride glass fiber strength from research on improved glass and fiber processing are summarized in Figure 18.³³ The data shown are for work over a period of about two years on fibers of the same Mg-Si-Al-O-N glass composition. The tensile strength increases are mostly attributable to improved process chemistry. Steps found to be particularly important include: (1) The elimination of undesirable impurities, specifically Fe and metallic Al, (2) Premelting of the oxide part of the glass in air before adding Si₃N₄ and melting in N₂, and (3) Double melting of the glass to improve homogeneity. The results shown in Figure 18 were admittedly obtained only for the purpose of improving our oxynitride glass fibers. It is not unreasonable, however, to speculate that similar considerations apply to the glassy grain boundary phase in sintered Si₃N₄. Along the same lines, it could be further argued that the properties of sintered Si₃N₄ could benefit from better control of the high temperature chemistry of the glass phase.

CONCLUSIONS

High temperature chemistry plays a crucial role in the processing and performance of Si₃N₄ and related materials. While high temperature reactions can produce problems such as critical defects in oxynitride glasses and fibers, they can also provide opportunities such as in the formation of Si₃N₄ composites containing in situ SiC whisker reinforcements. In any event, understanding and control of high temperature chemistry is essential to the fabrication of high performance composites and engineering ceramics.

ACKNOWLEDGMENTS

This report would have been impossible without the help of my coworkers over the years, most of whom are cited in the references, and to all of whom I am deeply grateful. A special thanks is due to the Engineering Ceramics Division of the American Ceramic Society for inviting me to present the Mueller Lecture, and with whom I have had a long and rewarding association.

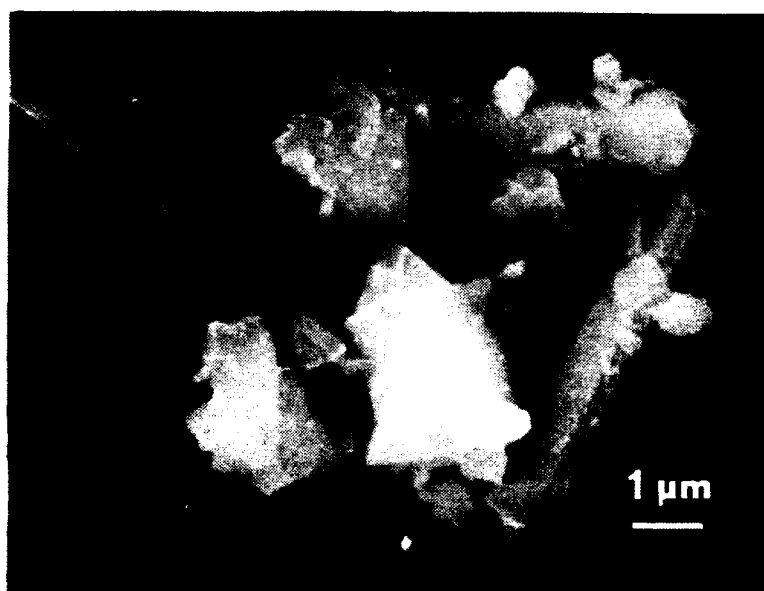


Figure 1. 99% pure α -silicon nitride powder as-received, scanning electron photomicrograph, Ref. 13.

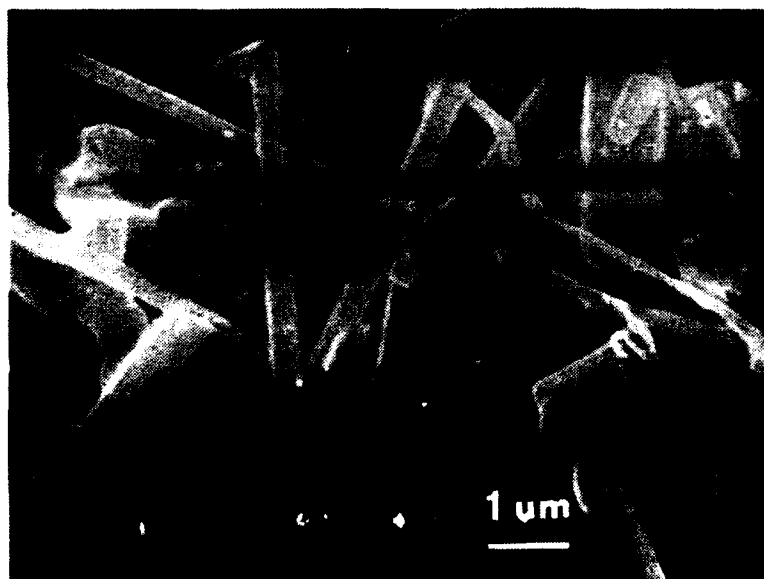


Figure 2. Silicon carbide whiskers in silicon nitride powder after heat treatment at 1600°C in nitrogen contaminated with oxygen, scanning electron photomicrograph, Ref. 13.

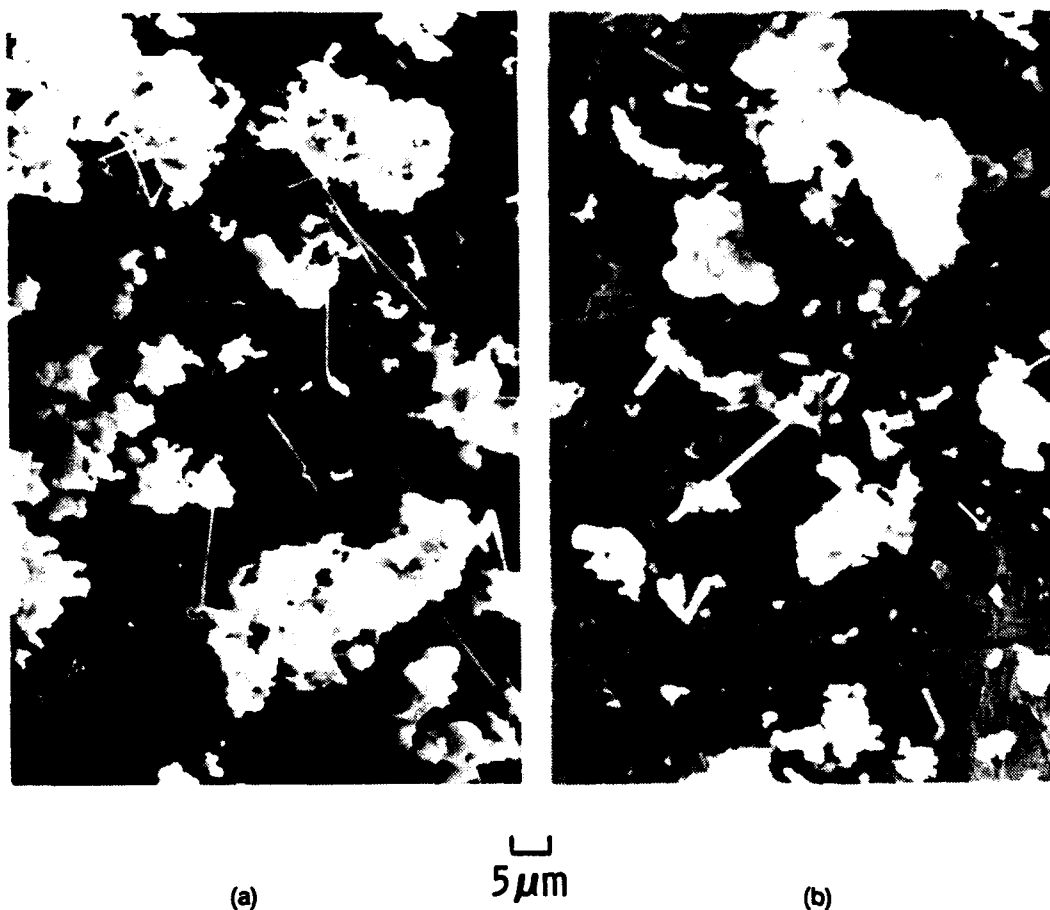


Figure 3. (a) Silicon carbide whiskers in silicon nitride powder heated for four hours at 1600°C in nitrogen contaminated with oxygen, and (b) silicon nitride powder heated without additives for 10 hours at 1600°C in pure nitrogen, scanning electron photomicrographs, Ref. 12.

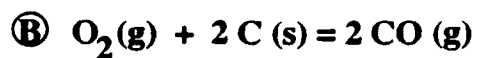
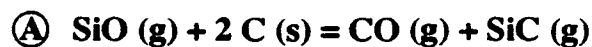
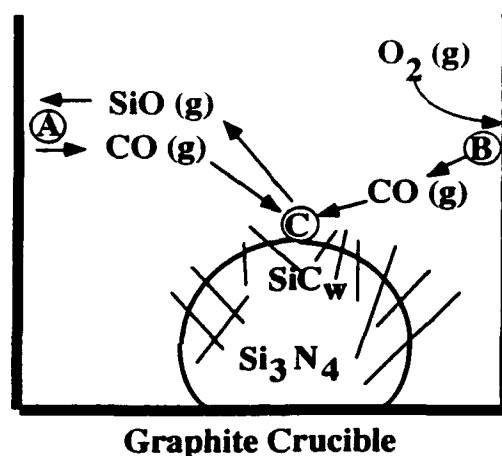


Figure 4. Mechanism for silicon carbide formation in a silicon nitride powder compact.

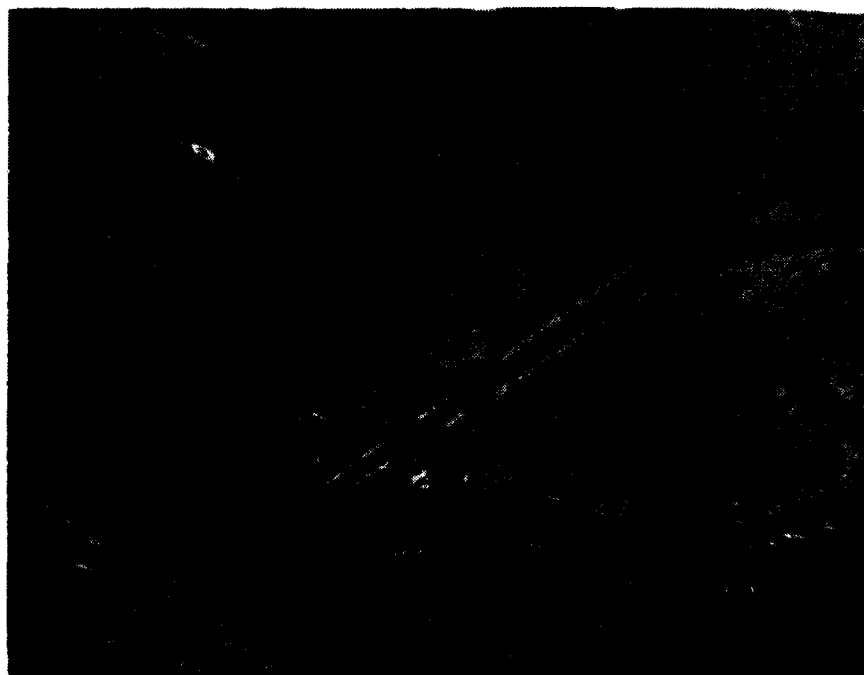


Figure 5. α -silicon nitride whiskers formed during reaction bonding of a silicon powder compact. The drops at the tips of the whiskers suggest that growth occurred by a VLS mechanism, optical photomicrograph, transmitted light, Ref. 18.

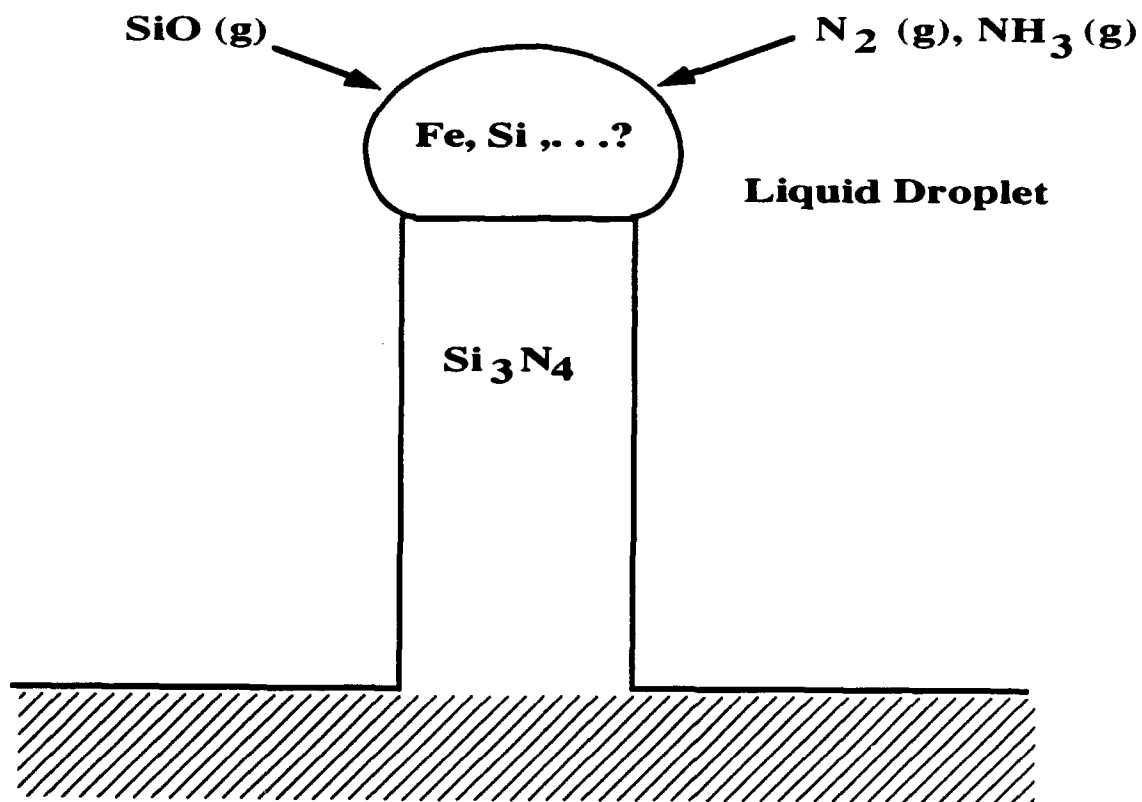
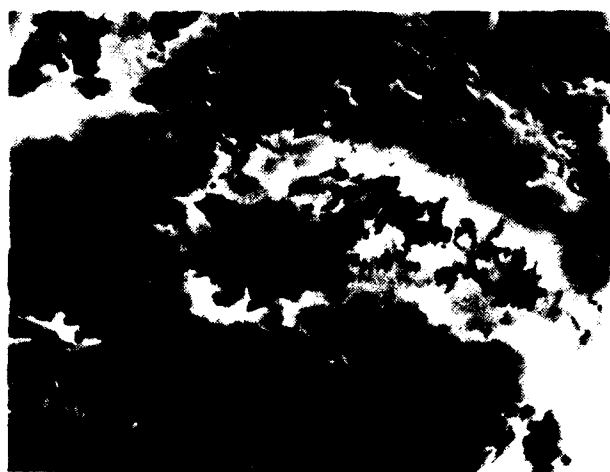
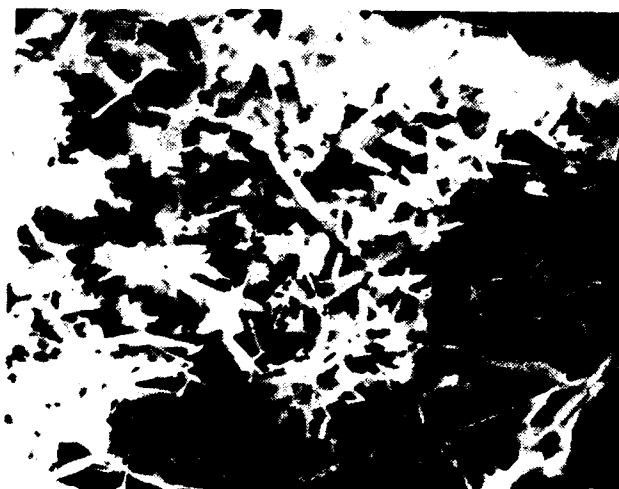


Figure 6. Growth of α -silicon nitride whiskers by the VLS mechanism.



a. Mag. 1000X

10 μm



b. Mag. 2000X

10 μm

Figure 7. Fracture section of a reaction bonded silicon nitride specimen showing extensive whisker formation in voids, scanning electron photomicrographs, Ref. 20.



Figure 8. Silicon nitride powder containing 10 wt% magnesia at various stages of the α to β transformation after heat treatment at 1600°C. (a) and (b): 0.5 hour, 47 wt% β . (c) and (d): 1.0 hour, 64 wt% β . (e) and (f): 4.0 hour, 100% β , scanning electron photomicrographs, Ref. 13.

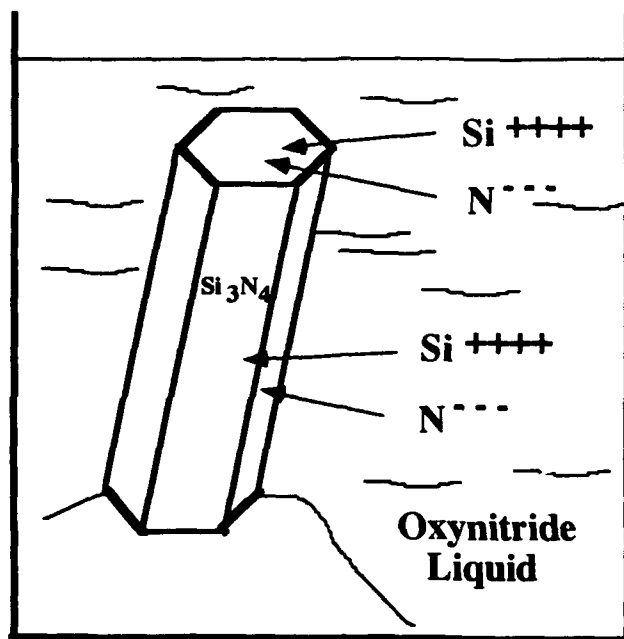


Figure 9. Growth of high aspect ratio β silicon nitride crystals from the liquid. The aspect ratio depends upon the chemistry of the liquid.

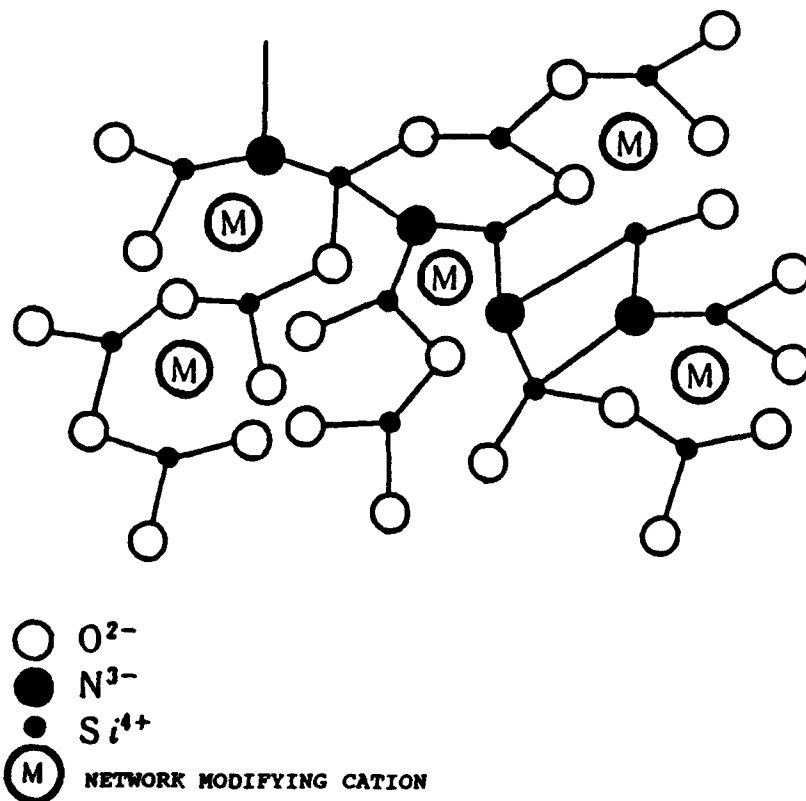
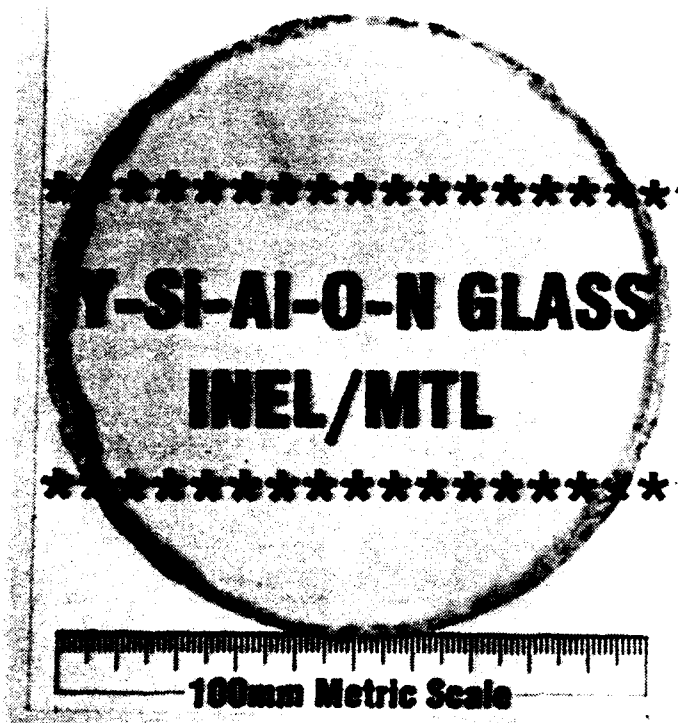


Figure 10. Schematic two-dimensional view of the network structure of oxynitride glasses based on metal-silicon-oxygen systems, Ref. 26.



(a)



(b)

Figure 11. Y-Si-Al-O-N Glass disks, 100 mm diameter x 10 mm thick. The black, cloudy regions in (b) stem from metallic inclusions (the glass was made under high nitrogen pressure by Ref. 28).

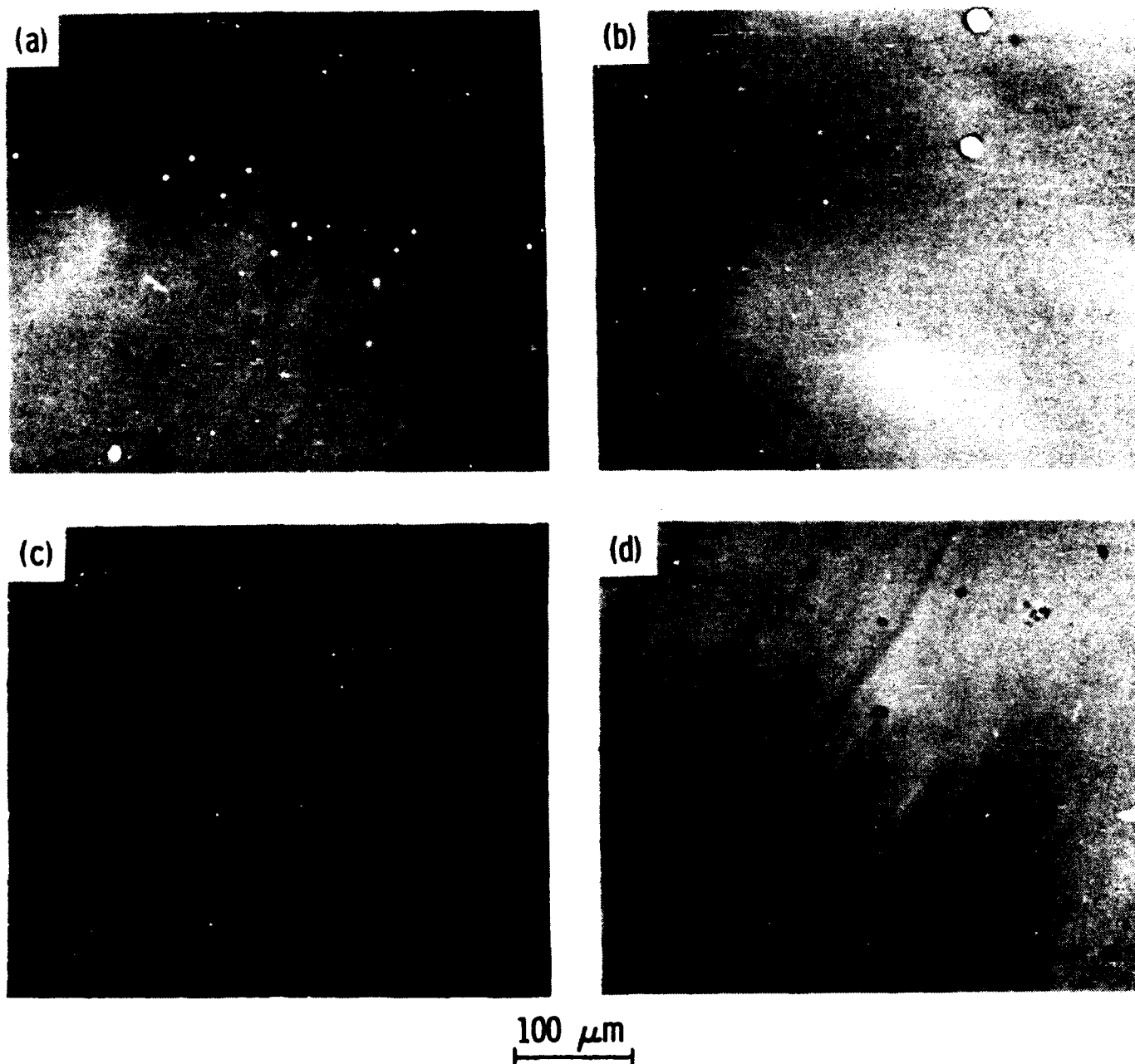
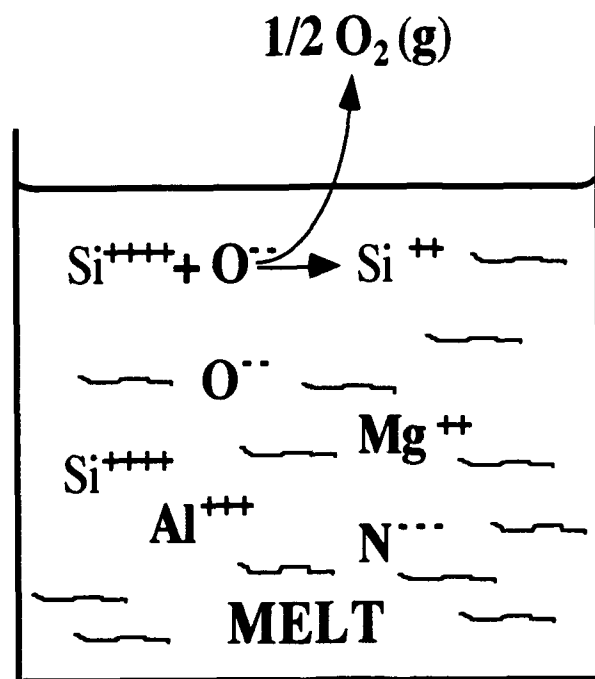
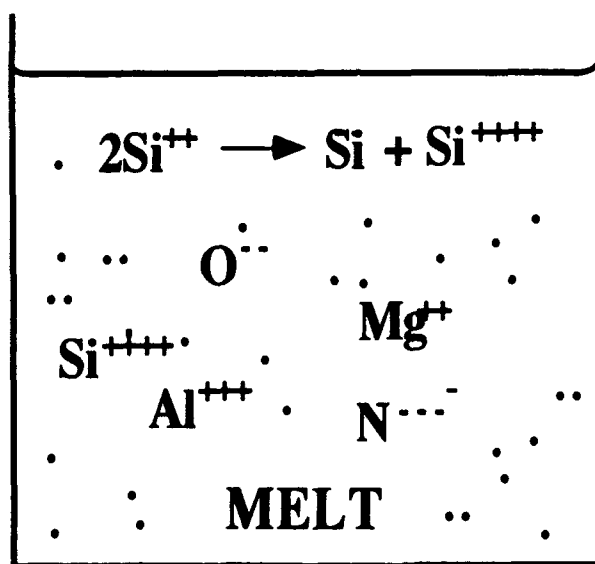


Figure 12. Photomicrographs of polished sections of Y-Si-Al-O-N glass specimens prepared under various conditions: (a) with low purity silicon nitride, (b) with high purity silicon nitride, (c) with low purity silicon nitride at high nitrogen pressure, and (d) with aluminum nitride. The bright spots appearing to some extent or another in all of the specimens represent silicon-rich metallic inclusions, optical photomicrographs, Ref. 29.



(a) Heating



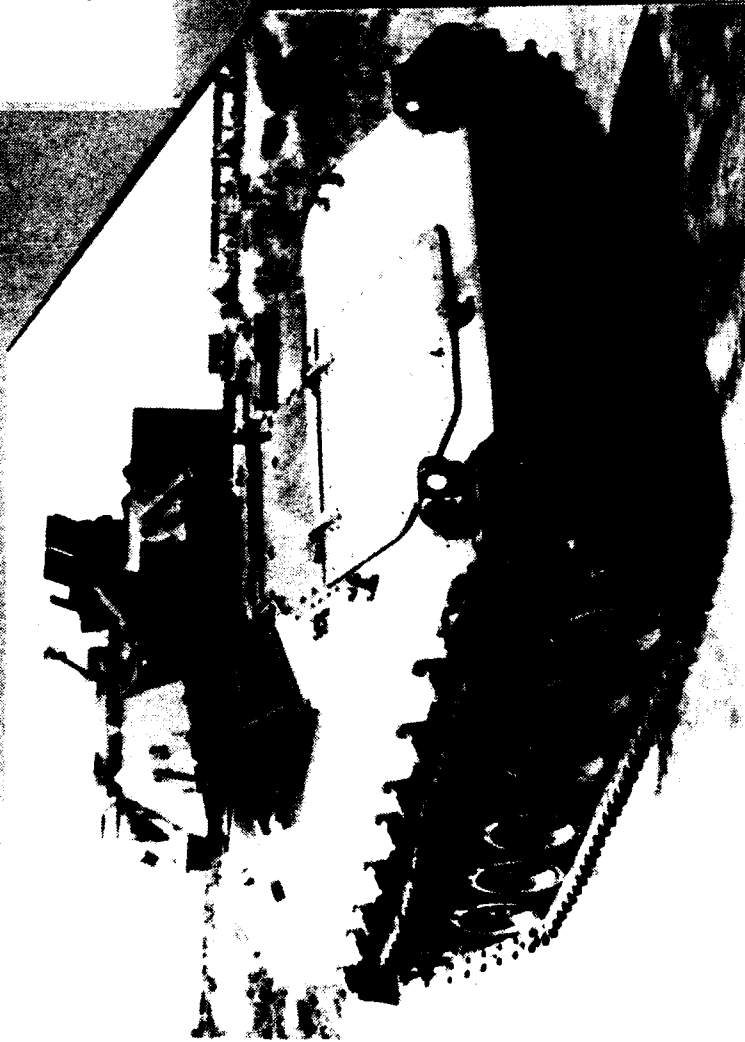
(b) Cooling

Figure 13. Mechanism for the formation of metallic precipitates in oxynitride glass; after Ref. 30 through Ref. 32.

OXYNITRIDE GLASS FIBERS

ARMY REQUIREMENT:

- IMPROVED COMPOSITE ARMOR FOR FIGHTING VEHICLES



COMPOSITE IFV HULL TECHNOLOGY DEMONSTRATOR

- SUPERIOR TO OXIDE GLASSES
- HIGH ELASTIC MODULUS
- HIGH STRENGTH
- EXCELLENT CORROSION RESISTANCE
- INCREASED PERFORMANCE/
REDUCED WEIGHT

MODULUS/DENSITY FOR SIMILAR GLASSES
WITH AND WITHOUT NITROGEN

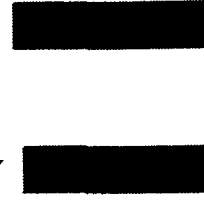


Figure 14. Potential U.S. Army application for oxynitride glass fibers.

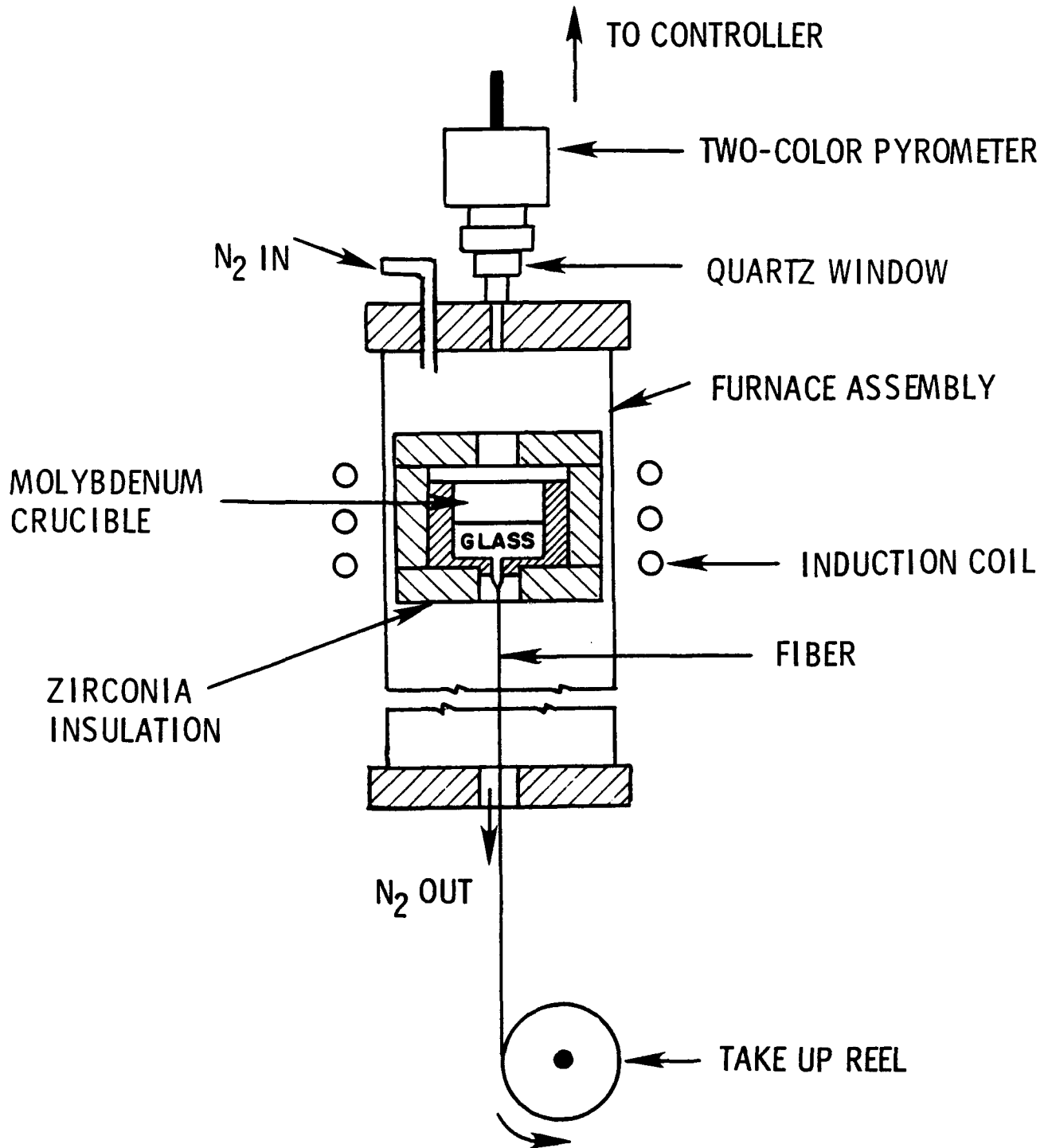


Figure 15. Schematic representation of the system employed for drawing oxynitride glass fibers, Ref. 33.

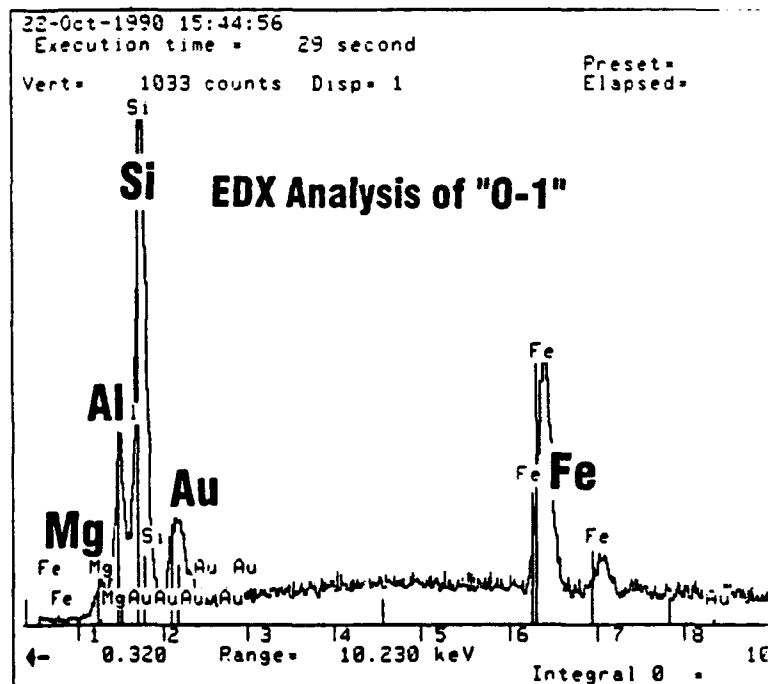
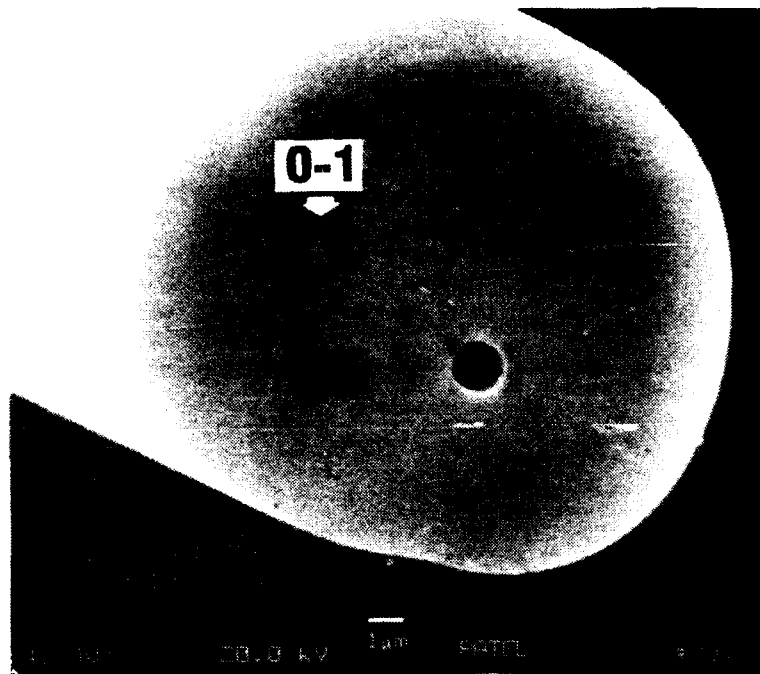


Figure 16. Mg-Si-Al-O-N fiber fracture surface showing a critical defect high in iron. It was later found that this and similar defects came from contamination in the acetone used to wet mix the batch. Axial voids such as the one clearly evident were sometimes observed; the voids are not strength-limiting, scanning electron photomicrograph, Messier and Patel, unpublished work.

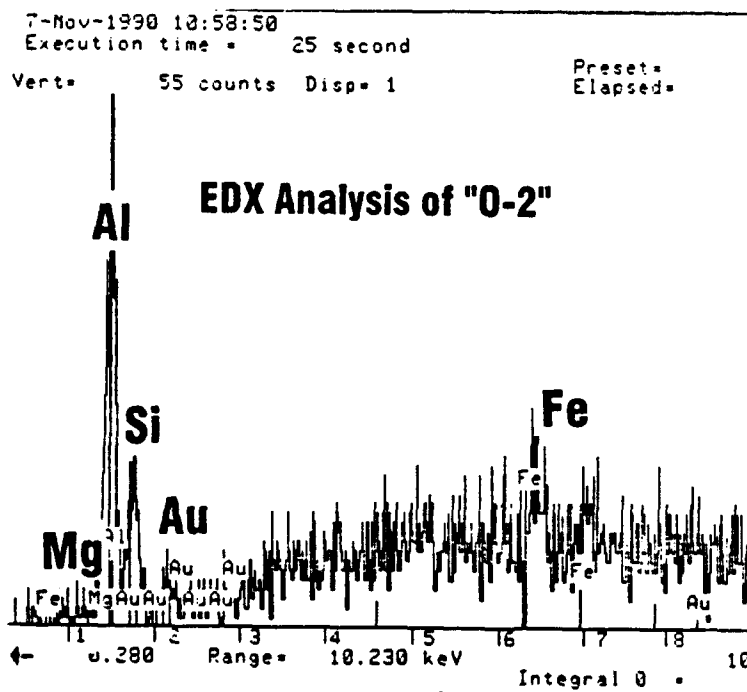
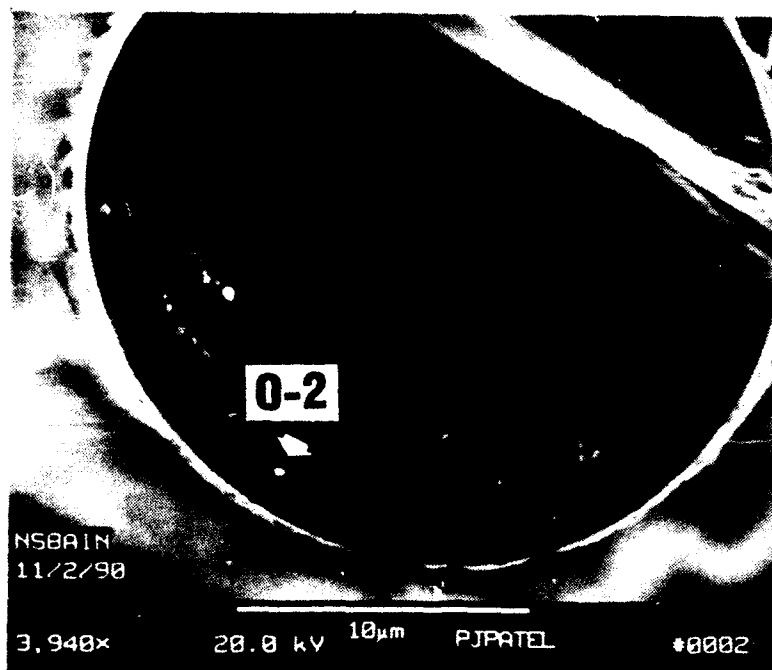


Figure 17. Mg-Si-Al-O-N fiber fracture surface showing a critical defect rich in aluminum believed to be from unreacted metal in the aluminum nitride used as a batch component, scanning electron photomicrograph, Messier and Patel, unpublished work.

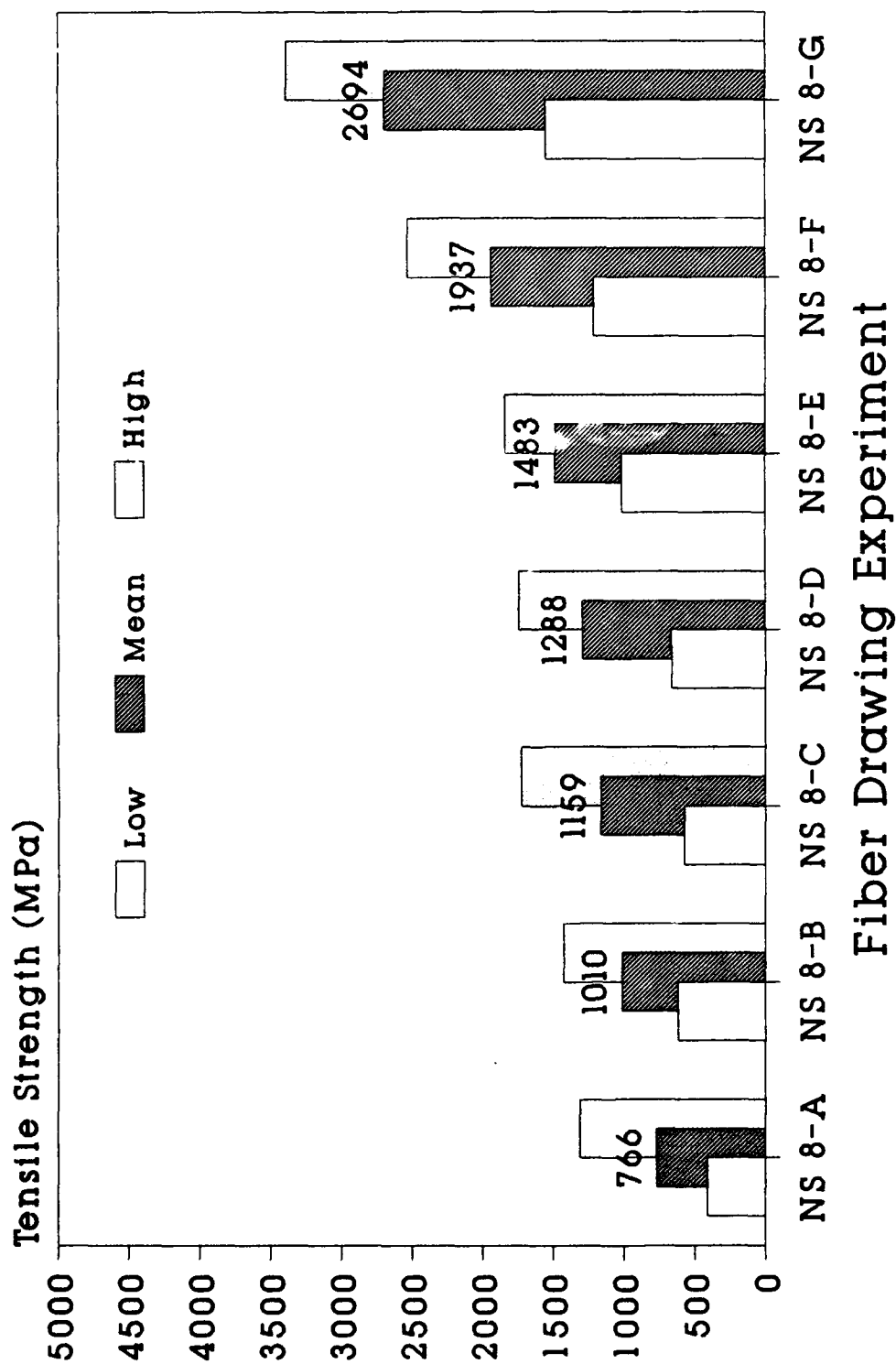


Figure 18. Tensile strength increases resulting from processing improvements. All data are for Mg-Si-Al-O-N fibers of the same nominal composition, Ref. 33.

REFERENCES

1. ATWELL, W. H., FOLEY, P., HAUTH, W. E., JONES, R. E., LANGLEY, N. R., and SALINGER, R. M. *Advanced Ceramics Based on Polymer Processing*. v. I and II, WRDC-TR-89-450, July 1989.
2. MESSIER, D. R. *Assessment of Japanese Technology in Advanced Glass and Ceramic Fibers*. U.S. Army Materials Technology Laboratory, MTL MS 92-1, June 1992.
3. BRENNAN, J. J., and PREWO, K. M. *Silicon Carbide Fiber-Reinforced Glass Ceramic Composites Exhibiting High Strength and Toughness*. J. Mater. Sci., v. 17, 1982, p. 2371-2383.
4. TAKEDA, M., IMAI, Y., ICHIKAWA, H., ISHIKAWA, T., SEGUCHI, T., and OKAMURA, K. *Properties of the Low Oxygen Content SiC Fiber on High Temperature Heat Treatment*. Ceram. Eng. Sci. Proc., v. 12, 1991, p. 1007-1018.
5. LIPOWITZ, J. *Polymer-Derived Ceramic Fibers*. Am. Ceram. Soc. Bull., v. 70, no. 12, 1991, p. 1888-1894.
6. YOKOYAMA, Y., NANBA, T., YASUI, I., KAYA, H., MAESHIMA, T., and ISODA, T. *X-ray Diffraction Study of the Structure of Silicon Nitride Fiber Made from Perhydropolysilazane*. J. Am. Ceram. Soc., v. 74, no. 3, 1991, p. 654-657.
7. STORM, R. S. *Recent Developments in Silicon Carbide Technology at the Carborundum Company*. Proc. First Int. Symp. Sci. Eng. Ceramics, S. Kimura and K. Niihara, eds., Ceramic Society of Japan, Tokyo, Japan, 1991, p. 51-56.
8. KIMURA, Y., HAYASHI, H., YAMANE, H., and KITAO, T. *High Performance Boron Nitride Fibers from Polyborazine Pre-Ceramics*. Proc. First Jap. Int. SAMPE Symp., 1989, p. 906-911.
9. Tateho Chemical Industries Co., Ltd. Technical Data Sheets on Si₃N₄ and SiC Whiskers. Ako-shi, Hyogo-ken, Japan.
10. KIDA, T., and YAMAMOTO, M. (Tokai Carbon Co., Ltd.) *Process for Preparing Silicon Carbide Whiskers*. U.S. Pat. No. 4,690,811, September 1, 1987.
11. American Matrix, Inc. Technical Data Sheets on SiC Whiskers, Knoxville, TN.
12. MESSIER, D. R., and RILEY, F. L. *The Alpha/Beta Silicon Nitride Phase Transformation*. Nitrogen Ceramics, F. L. Riley, ed., Noordhoff Publishing Co., Leyden, The Netherlands, 1977, p. 141-149.
13. MESSIER, D. R., RILEY, F. L., and BROOK, R. J. *The Alpha/Beta Silicon Nitride Phase Transformation*. J. Mater. Sci., v. 13, 1978, p. 1199-1205.
14. YAMADA, S., KIMURA, S., YASUDA, E., TANABE, T., and ASAMI, Y. *A Discussion of the Chemical Mixing Process for in situ Preparation of Silicon Carbide Whiskers in Silicon Nitride Powder*. J. Mater. Res., v. 3, 1988, p. 538-544.
15. WANG, H., and FISHMAN, G. S. *SiC Whisker/Si₃N₄ Composites by a Chemical Mixing Process*. Ceram. Eng. Sci. Proc., v. 12, 1991, p. 2135-2141.
16. SONG, S. T., and LIU, G. Z. *A Study on the Preparation and Properties of Self-Reinforced Si₃N₄ Matrix Composites*. Proc. Int. Symp. on the Science of Engineering Ceramics, 1991, p. 121-128.
17. COLQUHOUN, I., WILD, S., GRIEVESON, P., and JACK, K. H. *Thermodynamics of the Silicon-Oxygen-Nitrogen System*. Proc. Brit. Ceram. Soc., v. 22, p. 207-227.
18. MESSIER, D. R., and WONG, P. *Kinetics of Nitridation of Si Powder Compacts*. J. Am. Ceram. Soc., v. 56, no. 9, 1973, p. 480-485.
19. WAGNER, R. S., and ELLIS, W. C. *Vapor-Liquid-Solid Mechanism of Crystal Growth and Its Application to Silicon*. Trans. AIME, v. 233, no. 6, 1965, p. 1053-1064.
20. MESSIER, D. R., and WONG, P. *Duplex Ceramic Structures - Interim Report No. 1: Kinetics of Fabrication of Silicon Nitride by Reaction Sintering*. U. S. Army Materials Technology Laboratory, AMMRC TR 72-10, March 1972.
21. BUCKLEY, H. E. *Crystal Growth*. John Wiley and Sons Inc., New York, NY 1951.
22. PYZIK, A. J., and BEAMAN, D. R. *Processing, Microstructure and Properties of Self-Reinforced Si₃N₄*. 14th Conf. on Composites and Advanced Ceramics, 1990.
23. CARROLL, D. F., and PYZIK, A. J. *Microstructural/Mechanical Property Relationships in Self-Reinforced Si₃N₄*. 14th Conf. on Composites and Advanced Ceramics, 1990.
24. PYZIK, A. J., CARROLL, D. F., HWANG, C. J., and PRUNIER, A. F. *Self-Reinforced Silicon Nitride - A New Microengineered Ceramic*. Proc. Fourth Int. Conf. on Ceramic Materials for Engines, Goeteborg, Sweden, 1991.

25. MESSIER, D. R. *Oxynitride Glass Research at the U.S. Army Materials Technology Laboratory*. Am. Ceram. Soc. Bull., v. 68, no. 11, 1989, p. 1931-1936.
26. RISBUD, S. H. *Analysis of Bulk Amorphous Oxynitride Structures Using the Network Theory of Glasses*. Phys. Chem. Glasses, v. 22, no. 6, 1981, p. 168-170.
27. MESSIER, D. R. *Review of Oxynitride Glasses*. Rev. Chim. Min., v. 22, 1985, p. 518-533.
28. WEIDNER, J. R., NEILSON, R. M., JR., and RABIN, B.H. *Oxynitride Glass Technology for Armor and Composite Applications*. INEL, Report No. EGG-MS-8014, Idaho Falls, ID, March 1988.
29. MESSIER, D. R., and DeGUIRE, E. J. *Thermal Decomposition in the System Si-Y-Al-O-N*. J. Amer. Ceram. Soc., v. 67, no. 9, 1984, p. 602-605.
30. KELEN, T., and MOLFINGER, H. O. *Mechanismus der Chemischen Auflösung von Stickstoff in Glasschmelzen*. Glastechn. Ber., v. 41, no. 6, 1968, p. 230-242.
31. ZINTL, E. *Siliciummonoxyd*, Z. Anorg. Allgem. Chem., v. 245, no. 1, 1940, p. 1-7.
32. GELD, P. V., and ESIN, O. A. *Silicon Monoxide in Slags from Ferro-Alloy Furnaces*. J. Appl. Chem. USSR, v. 23, 1950, p. 1277-1283.
33. PATEL, P. J., MESSIER, D. R., and RICH, R. E. *Oxynitride Glass Fibers*. Technology 2001, NASA Conference Publication 3136, v. 2, 1991, p. 258-264.
34. AUBOURG, P. F., and WOLF, W. W. *Glass Fibers*. Advances in Ceramics, D.C. Boyd and J.F. MacDowell, eds., Am. Ceram. Soc., v. 18, p. 51-63, Columbus, OH, 1986.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1145
1	ATTN: AMSLC-IM-TL
1	AMSLC-CT
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145
2	ATTN: DTIC-FDAC
1	MIA/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCSCI
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
	Commander, U.S. Army Missile Command, Redstone Scientific Information Center, Redstone Arsenal, AL 35898-5241
1	ATTN: AMSMI-RD-CS-R/Doc
1	AMSMI-RLM
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
2	ATTN: Technical Library
	Commander, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5010
1	ATTN: Technical Library
	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library
	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library
	Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: SLCBR-TSB-S (STINFO)
	Commander, Dugway Proving Ground, UT 84022
1	ATTN: Technical Library, Technical Information Division
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: Technical Information Office
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396
3	ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library

No. of Copies	To
1	Commander, U.S. Army Aviation Systems Command, Aviation Research and Technology Activity, Aviation Applied Technology Directorate, Fort Eustis, VA 23604-5577 ATTN: SAVDL-E-MOS
1	U.S. Army Aviation Training Library, Fort Rucker, AL 36360 ATTN: Building 5906-5907
1	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362 ATTN: Technical Library
1	Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916 ATTN: Technical Library
1	Commander, Clarke Engineer School Library, 3202 Nebraska Ave., N, Ft. Leonard Wood, MO 65473-5000 ATTN: Library
1	Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180 ATTN: Research Center Library
1	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801 ATTN: Quartermaster School Library
1	Naval Research Laboratory, Washington, DC 20375 ATTN: Code 5830
2	Dr. G. R. Yoder - Code 6384
1	Chief of Naval Research, Arlington, VA 22217 ATTN: Code 471
1	Code 431, Dr R. C. Pahanka
1	Edward J. Morrissey, WRDC/MLTE, Wright-Patterson Air Force Base, OH 45433-6523
1	Commander, U.S. Air Force Wright Research & Development Center, Wright-Patterson Air Force Base, OH 45433-6523 ATTN: WRDC/MLLP, M. Fomey, Jr.
1	WRDC/MLBC, Mr. Stanley Schulman
1	NASA - Marshall Space Flight Center, MSFC, AL 35812 ATTN: Mr. Paul Schuerer/EH01
1	U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899 ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering
1	Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418
1	Materials Sciences Corporation, Suite 250, 500 Office Center Drive, Fort Washington, PA 19034-3213
1	Charles Stark Draper Laboratory, 68 Albany Street, Cambridge, MA 02139
1	Wyman-Gordon Company, Worcester, MA 01601 ATTN: Technical Library
1	General Dynamics, Convair Aerospace Division P.O. Box 748, Fort Worth, TX 76101 ATTN: Mfg. Engineering Technical Library
1	Plastics Technical Evaluation Center, PLASTEC, ARDEC Bldg. 355N, Picatinny Arsenal, NJ 07806-5000 ATTN: Harry Pebly
1	Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity - AVSCOM, Langley Research Center, Hampton, VA 23665-5225
1	NASA - Langley Research Center, Hampton, VA 23665-5225
1	U.S. Army Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1	NASA - Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1	ATTN: Dr. S. Dutta

No. of Copies	To
1	PPG Industries, Inc., Fiber Glass Research Center, P.O. Box 2844, Pittsburgh, PA 15230
1	ATTN: Dr. A. Calabrese
1	Dr. J. Fletcher
1	Technical Center, Owens/Corning Fiberglas Corp., Granville, OH 43023
1	ATTN: Dr. W. W. Wolf
1	Massachusetts Institute of Technology, Cambridge, MA 02139
1	ATTN: Dr. J. S. Haggerty, 12-009
1	United Technologies Corp., Research Center, Silver Lane, E. Hartford, CT 06108
1	ATTN: Dr. W. H. Sutton
1	Dr. K. M. Prewo
1	Dr. J. J. Brennan
1	University of Missouri, Rolla Materials Research Center, Rolla, MO 65401
1	ATTN: Prof. D. E. Day
1	Rensselaer Polytechnic Institute, Department of Materials Engineering, Troy, NY 12181
1	ATTN: Prof. M. Tomozawa
1	Dr. W. B. Hillig
1	Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609
1	ATTN: Prof. G. L. Leatherman
1	Prof. T. El-Korchi
1	Dow Corning Corporation, Midland, MI 48696
1	ATTN: Mr. R. E. Jones
1	Mr. W. E. Hauth
1	Mr. W. H. Atwell
1	General Electric Co., Research and Development Center, Box 8, Schenectady, NY 12301
1	ATTN: Dr. R. J. Charles
1	Corning Glass Works, Corning, NY 14831
1	ATTN: Dr. J. R. Booth
1	Mr. D. E. Larsen
1	Dr. W. R. Prindle
1	Sandia National Laboratories, Albuquerque, NM 87185
1	ATTN: Dr. R. E. Loehman
1	3M Co., 3M Center, Bldg. 201, St. Paul, MN 55144
1	ATTN: Dr. M. Leitheiser
1	Allison Gas Turbine Division, General Motors Corporation, 4438 Clayburn Drive, Indianapolis, IN 46268
1	ATTN: Dr. P. Khandelwal
1	University of Delaware, Spencer Laboratory, Newark, DE 19716
1	ATTN: Prof. A. P. Majidi
1	EG&G Idaho, INEL, Idaho Falls, ID 83415
1	ATTN: Dr. R. M. Neilson, Jr.
1	SUNY, College of Ceramics, Alfred, NY 14802
1	ATTN: Prof. D. L. Pye
1	Dean J. W. McCauley
1	FMC Corp., Central Engineering Laboratories, 1205 Coleman Avenue, Box 580, Santa Clara, CA 95052
1	ATTN: Dr. A. Vasudev
1	U.S. Army Research, Development and Standardization Group (UK), Box 65, FPO, New York 09510
1	ATTN: Dr. W. C. Simmons
1	GTE Laboratories, Inc., 40 Sylvan Road, Waltham, MA 02154
1	ATTN: Dr. S. T. Buljan
1	Dr. A. E. Pasto
1	Norton Co., High Performance Ceramics, Goddard Road, Northboro, MA 01532-1545
1	ATTN: Mr. N. D. Corbin
1	Dr. S. D. Hartline

No. of Copies	To
1	University of California, Santa Barbara, CA 93106 ATTN: Prof. A. G. Evans
1	Georgia Tech Research Institute, Atlanta, GA 30332 ATTN: Dr. W. J. Lackey
1	Universal Energy Systems, 4401 Dayton-Xenia Road, Dayton, OH 45432 ATTN: Dr. T. Mah
1	Rockwell International, 1049 Camino Dos Rios, P.O. Box 1085, Thousand Oaks, CA 91360 ATTN: Dr. P. E. D. Morgan
1	W. R. Grace and Co., 7379 Route 32, Columbia, MD 21044 ATTN: Mr. R. W. Rice
1	Coors Ceramics Co., 17750 West 32nd Ave., Golden, CO 80401 ATTN: Dr. J. Stephan
1	Dr. D. W. Roy
1	Dr. R. Paricio
1	U.S. Department of Energy, Forrestal Building CE-151, 1000 Independence Ave., Washington, DC 20585 ATTN: Mr. R. B. Schulz
1	Center for Advanced Ceramic Technology, Alfred University, Alfred, NY 14802 ATTN: Dr. R. M. Spriggs
1	Carborundum Co., P.O. Box 832, Niagara Falls, NY 14302 ATTN: Dr. J. Hinton
1	The American Ceramic Society, Inc., 757 Brooksedge Plaza Drive, Westerville, OH 43081-6136 ATTN: Ms. L. M. Sheppard
1	University of Michigan, Dow Building, Ann Arbor, MI 48109-2136 ATTN: Prof. T. Y. Tien
1	Pennsylvania State University, 201 Steidle Bldg., University Park, PA 16802 ATTN: Prof. R. E. Tressler
1	TRW, Inc., Valve Division, 1455 E. 185th Street, Cleveland, OH 44110 ATTN: Dr. R. R. Wills
2	U.S. Army Materials Technology Laboratory, Watertown, Massachusetts 02172-0001 ATTN: SLCMT-TML, Technical Library
1	Author

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
HIGH TEMPERATURE CHEMISTRY OF FIBERS
AND COMPOSITES-
Donald R. Messier

AD UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Fibers
Composites
Ceramics

Technical Report MTL TR 92-62, September 1992, 27 pp-
illus-tables, D/A Project: IL811102.AH42

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form *in situ* composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
HIGH TEMPERATURE CHEMISTRY OF FIBERS
AND COMPOSITES-
Donald R. Messier

AD UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Fibers
Composites
Ceramics

Technical Report MTL TR 92-62, September 1992, 27 pp-
illus-tables, D/A Project: IL811102.AH42

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form *in situ* composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
HIGH TEMPERATURE CHEMISTRY OF FIBERS
AND COMPOSITES-
Donald R. Messier

AD UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Fibers
Composites
Ceramics

Technical Report MTL TR 92-62, September 1992, 27 pp-
illus-tables, D/A Project: IL811102.AH42

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form *in situ* composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
HIGH TEMPERATURE CHEMISTRY OF FIBERS
AND COMPOSITES-
Donald R. Messier

AD UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Fibers
Composites
Ceramics

Technical Report MTL TR 92-62, September 1992, 27 pp-
illus-tables, D/A Project: IL811102.AH42

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form *in situ* composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.